

DIRECTIONALLY SOLIDIFIED EUTECTIC SUPERALLOYS  
FOR ELEVATED TEMPERATURE APPLICATIONS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH AND  
DEVELOPMENT

[0001] The U.S. Government may have certain rights in the present invention pursuant to U.S. Air Force Prime Contract No. F33615-98-C-2807, Subcontract No. 01-S441-58-05-C1.

FIELD OF THE INVENTION

[0002] The present invention relates generally to directionally solidified eutectic superalloys for elevated temperature applications, such as turbine airfoil applications and the like. More specifically, the present invention relates to directionally solidified eutectic nickel (Ni)-based superalloys comprising a matrix containing an aligned carbide reinforcing fibrous phase, such as an aligned tantalum carbide (TaC) reinforcing fibrous phase. The aligned carbide reinforcing fibrous phase provides preferential strengthening in one direction, resulting in enhanced elevated temperature strength, creep resistance, oxidation resistance, and corrosion resistance properties.

BACKGROUND OF THE INVENTION

[0003] Directionally solidified eutectic Ni-based superalloys, such as NiTaC-14B and the like, are well known to those of ordinary skill in the art. For example, NiTaC-14B has been optimized for use in turbine airfoil applications due to its favorable elevated temperature strength, creep resistance, oxidation resistance, and corrosion resistance properties.

[0004] U.S. Patent No. 3,904,402 (Smashey) broadly discloses Ni-based alloys containing rhenium (Re) and a carbide reinforcing fibrous phase exhibiting

favorable elevated temperature strength, creep resistance, oxidation resistance, and corrosion resistance properties. Smashey discloses the preferred use of 4-7 wt.% vanadium (V) for enhancement of the carbide reinforcing fibrous phase, as well as matrix strengthening. Smashey discloses the limited use of molybdenum (Mo), up to about 3 wt.%, however, the use of Mo is preferably omitted. Smashey also discloses the limited use of tungsten (W), between about 2-4 wt.%.

[0005] U.S. Patent No. 4,284,430 (Henry) discloses a unidirectionally solidified anisotropic metallic composite body exhibiting transverse ductility and elevated temperature strength properties comprising a eutectic Ni-based superalloy containing about 2-9 wt.% Re, less than about 0.8 wt.% titanium (Ti), at least about 2 wt.% Mo, and less than about 1 wt.% V. Embedded in the matrix is an aligned carbide reinforcing fibrous phase, preferably a predominantly TaC reinforcing fibrous phase. Specifically, the Ni-based alloys contain about 2-9 wt.% Re, about 0-0.8 wt.% Ti, about 0-10 wt.% chromium (Cr), about 0-10 wt.% aluminum (Al), about 3-15 wt.% tantalum (Ta), about 0.1-1 wt.% carbon (C), about 0-10 wt.% cobalt (Co), about 0-10 wt.% W, about 0-1 wt.% V, about 2-10 wt.% Mo, and about 0-3 wt.% niobium (Nb) (columbium (Cb)), the balance being essentially Ni and incidental impurities.

[0006] U.S. Patent No. 4,292,076 (Gigliotti et al.) discloses a unidirectionally solidified anisotropic metallic composite body exhibiting transverse ductility and elevated temperature strength properties comprising a eutectic Ni-based refractory metal-monocarbide-reinforced superalloy containing boron (B). A reinforcing fibrous phase of the eutectic Ni-based superalloy is an aligned carbide reinforcing fibrous phase, preferably one selected from the monocarbides of Ti, V, Nb (Cb), zirconium (Zr), hafnium (Hf), Ta, and alloys or mixtures thereof. Specifically, the Ni-based alloys contain about 0.5-7 wt.% Re, less than about 0.8 wt.% Ti, and at least an amount in excess of an impurity amount of B. Embedded in the matrix is an aligned carbide reinforcing fibrous phase, preferably a predominantly TaC reinforcing fibrous phase. These Ni-based alloys exhibit favorable elevated temperature strength, creep resistance, oxidation resistance, and corrosion resistance properties. More specifically, the Ni-based alloys contain about 0.5-7 wt.% Re, less than about 0.8 wt.%

Ti, about 0.001-0.02 wt.% B, about 2-8 wt.% Cr, about 4-7 wt.% Al, about 5-13 wt.% Ta, about 0.1-0.7 wt.% C, less than about 5 wt.% Co, less than about 6 wt.% W, less than about 0.2 wt.% V, less than about 5 wt.% Mo, less than about 1 wt.% Nb (Cb), less than about 0.15 wt.% Hf, and less than about 0.15 wt.% Zr, the balance being essentially Ni and incidental impurities.

[0007] Conventional Ni-based superalloys lose strength at very high temperatures due to the fact that the gamma prime strengthening phase begins to dissolve. The addition of an aligned carbide reinforcing fibrous phase provides an important strengthening mechanism in this temperature regime. This is especially important for turbine airfoil applications and the like. The directionally solidified eutectic Ni-based superalloys described above, however, still do not demonstrate the elevated temperature strength, creep resistance, oxidation resistance, and corrosion resistance properties desired at these very high temperatures, performing better than their single crystal counterparts in a temperature regime of only about 100 degrees F greater. More benefit is required given the cost of producing directionally solidified eutectic Ni-based superalloys (due to their relatively slow directional solidification rates) versus their single crystal counterparts. Thus, what is needed is a directionally solidified eutectic Ni-based superalloy that demonstrates enhanced elevated temperature strength, creep resistance, oxidation resistance, and corrosion resistance properties.

#### BRIEF SUMMARY OF THE INVENTION

[0008] In one embodiment of the present invention, an alloy includes a Ni-based matrix comprising, on a weight basis, about 5-7% Al, up to about 0.025% B, about 0.1-0.5% C, about 3-13% Co, about 2-7% Cr, up to about 5% Mo, up to about 1% Nb, about 2-7% Re, about 10-13% Ta, up to about 1.8% Ti, about 4-7% W, up to about 1% V, up to about 0.2% Hf, and up to about 0.1% Zr, the balance being essentially Ni and incidental impurities.

[0009] In another embodiment of the present invention, a directionally solidified eutectic superalloy includes a Ni-based matrix comprising, on a weight basis, about 5-7% Al, up to about 0.025% B, about 0.1-0.5% C, about 3-13% Co, about 2-7% Cr, up to about 5% Mo, up to about 1% Nb, about 2-7% Re, about 10-13% Ta, up to about 1.8% Ti, about 4-7% W, up to about 1% V, up to about 0.2% Hf, and up to about 0.1% Zr, the balance being essentially Ni and incidental impurities; and an aligned eutectic reinforcing fibrous phase disposed within the Ni-based matrix, the aligned eutectic reinforcing fibrous phase comprising a carbide.

[0010] In a further embodiment of the present invention, an article of manufacture comprising an alloy includes a Ni-based matrix comprising, on a weight basis, about 5-7% Al, up to about 0.025% B, about 0.1-0.5% C, about 3-13% Co, about 2-7% Cr, up to about 5% Mo, up to about 1% Nb, about 2-7% Re, about 10-13% Ta, up to about 1.8% Ti, about 4-7% W, up to about 1% V, up to about 0.2% Hf, and up to about 0.1% Zr, the balance being essentially Ni and incidental impurities.

[0011] In a still further embodiment of the present invention, an article of manufacture comprising a directionally solidified eutectic superalloy includes a Ni-based matrix comprising, on a weight basis, about 5-7% Al, up to about 0.025% B, about 0.1-0.5% C, about 3-13% Co, about 2-7% Cr, up to about 5% Mo, up to about 1% Nb, about 2-7% Re, about 10-13% Ta, up to about 1.8% Ti, about 4-7% W, up to about 1% V, up to about 0.2% Hf, and up to about 0.1% Zr, the balance being essentially Ni and incidental impurities; and an aligned eutectic reinforcing fibrous phase disposed within the Ni-based matrix, the aligned eutectic reinforcing fibrous phase comprising a carbide.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 is a plot of the temperature in the liquid in front of the solid/liquid interface for several variations of furnace parameters related to several directional solidification runs;

[0013] Figure 2 is a photograph of a microstructure produced using the compositions and methods of the present invention, specifically NiTaC-14B with a light gamma prime etch showing the size of the TaC fibers and the matrix gamma and gamma prime phases;

[0014] Figure 3 is a photograph of a microstructure produced using the compositions and methods of the present invention, specifically NiTaC-14B with a deep gamma prime etch showing the TaC fiber morphology in the grain centers;

[0015] Figure 4 is a photograph of a microstructure produced using the compositions and methods of the present invention, specifically NiTaC-14B with a medium gamma prime etch showing the TaC fiber morphology in the grain boundaries;

[0016] Figure 5 is a photograph of a microstructure produced using the compositions and methods of the present invention, specifically NiTaC-14B with a very deep gamma prime etch showing the high aspect ratio of the TaC fibers;

[0017] Figure 6 is a plot of the cyclic oxidation results associated with the compositions of the present invention using 61-min cycles to 982 degrees C;

[0018] Figure 7 is a plot of the creep-rupture results associated with the compositions of the present invention for testing at 871 degrees C (1600 degrees F);

[0019] Figure 8 is a plot of the creep-rupture results associated with the compositions of the present invention for testing at 982 degrees C (1800 degrees F);

[0020] Figure 9 is a plot of the creep curves for the compositions of the present invention for testing at 871 degrees C;

[0021] Figure 10 is a plot of the creep curves for the compositions of the present invention for testing at 982 degrees C; and

[0022] Figure 11 is a Larson-Miller parameter plot for time-to-failure in the creep-rupture tests described above.

#### DETAILED DESCRIPTION OF THE INVENTION

[0023] As described above, the elevated temperature viability of directionally solidified eutectic Ni-based superalloys, such as NiTaC-14B and the like, has been established, however, two key issues remain. First, the relatively low value of maximum directional solidification rate makes the cost of producing components, such as turbine airfoils and the like, from such directionally solidified eutectic Ni-based superalloys too high. Second, the properties of NiTaC-14B and the like still fall short of assumed goals. For example, in some applications it is desired that a directionally solidified eutectic Ni-based superalloy demonstrate elevated temperature strength, creep resistance, oxidation resistance, and corrosion resistance properties similar to SC RenéN5 in a temperature regime of about 200 degrees F greater. In general, NiTaC-14B demonstrates a good balance of elevated temperature properties and has been shown to be superior to CoTaC,  $\gamma/\gamma'$ - $\delta$ , and  $\gamma/\gamma'$ -Mo systems.

[0024] Here three alternative directionally solidified eutectic Ni-based superalloys are presented. The compositions of these three directionally solidified eutectic Ni-based superalloys are provided in Table 1.

Element	Weight Percent			
	NiTaC-14B	AG207	AG208	AG209
Al	5.300	5.917	5.494	5.604
B	0.015	0.004	0.004	0.000
C	0.430	0.270	0.270	0.270
Co	3.800	7.158	11.944	6.764
Cr	3.800	6.681	4.013	2.561
Mo	3.000	1.432	1.338	0.580
Nb	0.000	0.000	0.000	0.534
Ni	61.555	60.537	55.217	61.102
Re	6.400	2.863	5.160	5.314
Ta	11.400	10.366	11.065	10.018
Ti	0.000	0.000	0.000	1.069
W	4.300	4.772	5.494	6.184

Table 1. Directionally Solidified Eutectic Ni-Based Superalloy Compositions

[0025] AG207 is designed to yield TaC fibers in a matrix of RenéN5, AG208 is designed to yield TaC fibers in a matrix of RenéN6, and AG209 is designed to yield TaC fibers in a matrix of CMSX-10Ri. All three compositions are designed to be slightly hypereutectic so as to provide good, aligned fibers when the exact eutectic composition is not known. In general, the compositions may be described as: AG207 (Ni-5.9Al-0.004B-0.27C-7.2Co-6.7Cr-1.4Mo-2.9Re-10.4Ta-4.8W by wt.%), AG208 (Ni-5.5Al-0.004B-0.27C-11.9Co-4Cr-1.3Mo-5.2Re-11.1Ta-5.5W by wt.%), and AG209 (Ni-5.6Al-0.27C-6.8Co-2.6Cr-0.6Mo-0.5Nb-5.3Re-10Ta-1.1Ti-6.2W by wt.%).

[0026] A furnace, such as a modified Bridgman apparatus or the like, is used to perform directional solidification. For example, the furnace may use a gradient wound alumina-tube furnace as a heating element with a water-cooled chill on which an ingot sits during withdrawal.

[0027] A total of eighteen directional solidification runs were conducted using the compositions and equipment described above. The conditions and resulting microstructures of the eighteen ingots are provided in Table 2.

DS Run No.	Alloy	Ingot Diameter (mm)	DS Rate (cm/hr)	Structure
1	NiTaC-14B	9.5	0.64	dendritic
2	NiTaC-14B	9.5	1.27	cellular
3	NiTaC-14B	9.5	0.64	cellular
4	NiTaC-14B	9.5	1.27	cellular
5	NiTaC-14B	22.2	0.64	cellular
6	NiTaC-14B	22.2	0.64	cellular
7	AG208	9.5	0.64	fibrous
8	AG207	9.5	0.64	fibrous
9	AG209	9.5	0.64	cellular
10	NiTaC-14B	22.2	0.64	fibrous
11	AG209	9.5	0.64	fibrous
12	AG207	22.2	0.64	fibrous
13	AG208	22.2	0.64	dendritic
14	AG208	22.2	0.64	dendritic
15	NiTaC-14B	22.2	0.64	fibrous
16	AG208	9.5	0.64	fibrous
17	AG209	9.5	0.64	N/A
18	NiTaC-14B	9.5	1.27	cellular

Table 2. Conditions and Resulting Microstructures of Directionally Solidified Ingots

[0028] The first seven directional solidification runs produced an unacceptable microstructure. Two additional ingots were processed to measure the gradients in the liquid in front of the solid/liquid interface. Thermocouples were immersed in the liquid in front of the solid/liquid interface, lowered to just touch the solid/liquid interface, and then raised up in several increments while measuring temperature and position. These measurements were repeated for several combinations of furnace control parameters. The results are provided in Figure 1. From these measurements, furnace parameters were selected to maximize the gradient. In general, some of the 22 mm diameter ingots were run with a thermal gradient of about 55 degrees C/cm and some of the 22 mm diameter ingots were run with a thermal gradient of about 100 degrees C/cm. Thermal gradients were not measured for the 9.5 mm diameter ingots.

[0029] A good fibrous microstructure was obtained in at least one ingot of each composition directionally solidified at 0.64 cm/hr. The typical microstructures produced are shown in Figures 2-5 for NiTaC-14B. Figure 2, a cross-section perpendicular to the directional solidification direction, was prepared with a light gamma prime etch and shows the relative sizes of the TaC fibers, the discontinuous



gamma prime phase formed upon cooling, and the continuous gamma phase. Figure 3, a transverse view with a deep matrix etch, shows the morphology of the TaC fibers, each of the TaC fibers having a substantially square cross-sectional shape. Figure 4, a cross-section perpendicular to the directional solidification direction, was prepared with a medium matrix etch and shows that the morphology of the TaC fibers breaks down to plate-like in the grain boundaries. Figure 5, a cross-section perpendicular to the directional solidification direction, was prepared with a very deep matrix etch and shows the high aspect ratio of the TaC fibers. Also visible are minor variations in the cross-sectional size that likely result from local variations in the solidification rate.

[0030] Ingots with good, aligned fibers were machined to produce cyclic oxidation pins and creep-rupture bars. It should be noted that a higher gradient may be required to produce an aligned fibrous structure in AG208 and AG209 than is required in NiTaC-14B. The machined cyclic oxidation pins each had a diameter of about 2.5 mm and a length of about 35 mm. The pins were cycled between room temperature and about 982 degrees C (1800 degrees F) in a 61-min cycle with 50 min in the 982 degrees C-furnace and 11 min out of the 982 degrees C-furnace. The cyclic oxidation data are provided in Table 3.

NiTaC-14B (pin 1)		NiTaC-14B (pin 2)		AG207		AG208		AG209	
Hrs Cycl.	Wt. Change (mg/cm <sup>2</sup> )	Hrs Cycl.	Wt. Change (mg/cm <sup>2</sup> )	Hrs Cycl.	Wt. Change (mg/cm <sup>2</sup> )	Hrs Cycl.	Wt. Change (mg/cm <sup>2</sup> )	Hrs Cycl.	Wt. Change (mg/cm <sup>2</sup> )
22.4	0.35	22.4	0.32	27.5	0.39	27.5	0.31	25.4	0.45
53.9	0.54	53.9	0.51	51.9	0.39	51.9	0.31	47.8	0.64
82.4	0.54	82.4	0.54	77.3	0.55	77.3	0.38	73.2	0.64
107.8	0.67	107.8	1.02	101.7	0.39	101.7	0.38	148.4	0.55
125.1	0.73	125.1	0.76	170.8	0.47	170.8	0.46		
197.2	0.79	197.2	0.86	269.4	0.31	269.4	0.61		
296.9	0.98	296.9	1.08	349.7	0.47	349.7	0.54		
366.0	0.76	366.0	0.67	448.4	0.55	448.4	0.77		
466.7	0.38	466.7	-0.25	519.5	0.47	519.5	0.85		
532.7	-0.35	532.7	-0.79	621.2	0.71	621.2	0.85		
630.3	-0.79	630.3	-1.08	695.4	0.63	695.4	0.77		
701.5	-1.08	701.5	-1.49	796.1	0.71	796.1	0.77		
804.2	-1.17	804.2	-1.37	871.3	0.63	871.3	0.77		
872.3	-1.78	872.3	-1.81	974.0	0.63	974.0	0.77		
976.0	-2.73	976.0	-3.97	1048.2	0.71	1048.2	0.85		
1047.2	-3.30	1047.2	-4.29	1145.8	0.79	1145.8	0.61		
1139.7	-4.06	1139.7	-5.53	1204.8	0.79	1204.8	0.61		

1219.0	-5.08	1219.0	-8.61	1278.0	0.79	1278.0	0.54		
1315.6	-6.00	1315.6	-13.51	1353.2	0.71	1353.2	0.46		
1384.7	-6.45	1384.7	-15.44						
1462.0	-7.43	1462.0	-20.15						
1535.2	-7.91	1535.2	-23.67						
1632.8	-9.08	1632.8	-26.57						
1707.0	-9.65	1707.0	-29.30						
1804.6	-10.70	1804.6	-33.46						
1879.8	-11.78	1879.8	-37.82						
1976.4	-13.11	1976.4	-43.54						
2050.6	-15.18	2050.6	-47.73						
2151.3	-16.80	2151.3	-52.72						
2226.5	-19.43	2226.5	-55.64						
2302.8	-22.73	2302.8	-59.77						
2380.0	-25.25	2380.0	-62.28						
2478.6	-29.15	2478.6	-66.73						
2602.7	-33.75	2602.7	-70.32						
2701.3	-39.24	2701.3	-74.46						
2775.5	-42.64	2775.5	-75.47						
2875.1	-49.85	2875.1	-79.48						
2970.7	-54.01	2970.7	-81.89						
3049.0	-59.37	3049.0	-83.42						
3125.2	-64.61	3125.2	-84.27						
3223.9	-69.53	3223.9	-85.45						
3319.4	-77.37	3319.4	-87.39						
3393.6	-81.34	3393.6	-87.80						
3470.9	-85.47	3470.9	-89.10						
3572.6	-89.50	3572.6	-89.84						
3641.7	-90.90	3641.7	-90.69						
3740.3	-92.55	3740.3	-92.28						
3820.6	-93.25	3820.6	-93.55						
3919.3	-93.92	3919.3	-95.40						
3990.4	-94.77	3990.4	-96.35						
4092.1	-94.90	4092.1	-98.92						
4166.3	-95.63	4166.3	-100.00						
4267.0	-96.23	4267.0	-101.43						

Table 3. Cyclic Oxidation Results (61-Min Cycles to 982 Degrees C)

[0031] The data of Table 3 demonstrates that the cyclic oxidation resistance of AG207 and AG208 is superior to that of NiTaC-14B. The cyclic oxidation results are plotted in Figure 6.

[0032] At least two creep-rupture tests were performed for each of the alloys of the present invention. The duration of the creep rupture tests ranged from about 22 hours to about 546 hours. The results are provided in Table 4.

Alloy	DS Rate (cm/hr)	Temp. (°C)	Stress (MPa)	Env.	Time to 0.2% (hr)	Time to 0.5% (hr)	Time to 1.0% (hr)	Time to 2.0% (hr)	Time to Fail (hr)	Strain at Fail (%)
AG207	0.64	871	455	air	1.2	9.0	18.9	33.5	109.1	17.1
AG207	0.64	982	283	air	0.9	6.7	15.3	21.3	22.2	3.2
AG208	0.64	871	455	air	2.1	17.5	41.3	92.1	545.6	24.1
AG208	0.64	982	283	air	1.3	17.5	62.2	101.9	177.4	15.4
AG209	0.64	871	455	air	27.3	56.0	99.7	159.2	414.0	17.4
AG209	0.64	982	283	air	4.6	20.7	61.5	142.7	222.5	17.7
NiTaC-14B	0.64	871	455	air	0.4	7.7	33.7	93.5	195.4	10.4
NiTaC-14B	0.64	982	283	air	0.2	3.8	22.3	94.2	126.1	12.0
NiTaC-14B	0.64	982	255	air	1.3	14.1	82.0	255.8	322.7	13.0
AG207	0.64	982	283	argon	1.3	6.0	18.0	31.0	49.9	13.3
AG207	0.64	1093	138	argon	9.6	25.6	42.8	57.6	61.3	12.6

Table 4. Creep Rupture Results

[0033] A comparison of the creep-rupture results is shown in Figure 7 for testing at 871 degrees C (1600 degrees F) and in Figure 8 for testing at 982 degrees C (1800 degrees F). The data of Table 4 demonstrates that the creep-resistance of AG208 and AG209 is superior to that of NiTaC-14B. AG208 is the superior alloy at 871 degrees C/455 MPa (1600 degrees F/66 ksi) and AG209 is the superior alloy at 982 degrees C/283 MPa (1800 degrees F/41 ksi). The creep curves in air are shown in Figures 9 and 10 for the testing at 871 degrees C and 982 degrees C, respectively.

[0034] The data for the alloys of the present invention are compared in Figure 11 via a Larson-Miller parameter plot for time-to-failure in the creep-rupture tests. In this construction, the Larson-Miller parameter, LMP, is defined as:

$$\text{LMP} = T [20 + \log_{10} (t_f)], \quad (1)$$

where  $T$  = temperature (K) and  $t_f$  = time to fail (hr). Figure 11 also contains the best fit line from data previously gathered for NiTaC-14B and a mathematical construct that represents a 20 degrees C increase above this data.

[0035] Although the present invention has been illustrated and described with reference to preferred embodiments and examples thereof, it will be readily apparent to those of ordinary skill in the art that other embodiments and examples may perform similar functions and/or achieve similar results. All such equivalent embodiments and examples are within the spirit and scope of the present invention and are intended to be covered by the following claims.